

FORM PTO-1390 (Modified) (REV 10-95)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER 11750-002001
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR) 09/509301
INTERNATIONAL APPLICATION NO. PCT/AU98/00811	INTERNATIONAL FILING DATE 25 September 1998	PRIORITY DATE CLAIMED 25 September 1997	
TITLE OF INVENTION ION EXCHANGE			
APPLICANT(S) FOR DO/EO/US JAY, William Harold			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<ol style="list-style-type: none"> <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1). <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c) (2)) <ol style="list-style-type: none"> <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). <input checked="" type="checkbox"/> has been transmitted by the International Bureau. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). <input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). <input type="checkbox"/> A copy of the International Search Report (PCT/ISA/210). <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3)) <ol style="list-style-type: none"> <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). <input type="checkbox"/> have been transmitted by the International Bureau. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. <input checked="" type="checkbox"/> have not been made and will not be made. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)). <input type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409). <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)). 			
Items 13 to 18 below concern document(s) or information included:			
<ol style="list-style-type: none"> <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. <input checked="" type="checkbox"/> A FIRST preliminary amendment. A SECOND or SUBSEQUENT preliminary amendment. <input type="checkbox"/> A substitute specification. <input type="checkbox"/> A change of power of attorney and/or address letter. <input checked="" type="checkbox"/> Certificate of Mailing by Express Mail <input type="checkbox"/> Other items or information: 			
<p>"Express Mail" label number: EL445347445US Date of Deposit : 23 March 2000 I hereby certify that under 37 CFR 1.10 that this correspondence is being deposited with the United States Postal Service as "Express Mail Post Office To Addressee" with sufficient postage on the date indicated above and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.</p> <p><i>Jonathan R. Howard</i></p>			

U.S. APPLICATION NO. (IF KNOWN SEE 37 CFR 09/509301)		INTERNATIONAL APPLICATION NO. PCT/AU98/00811		ATTORNEY'S DOCKET NUMBER 11750-002001	
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20. The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :				CALCULATIONS PTO USE ONLY	
<input type="checkbox"/>	Search Report has been prepared by the EPO or JPO	\$840.00			
<input type="checkbox"/>	International preliminary examination fee paid to USPTO (37 CFR 1.482)	\$670.00			
<input type="checkbox"/>	No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2))	\$760.00			
<input checked="" type="checkbox"/>	Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO	\$970.00			
<input type="checkbox"/>	International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)	\$96.00			
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$970.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				\$0.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	12 - 20 =	0	x \$18.00	\$0.00	
Independent claims	2 - 3 =	0	x \$78.00	\$0.00	
Multiple Dependent Claims (check if applicable) . <input type="checkbox"/>				\$0.00	
TOTAL OF ABOVE CALCULATIONS =				\$970.00	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable) . <input type="checkbox"/>				\$0.00	
SUBTOTAL =				\$970.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).				\$0.00	
TOTAL NATIONAL FEE =				\$970.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). <input type="checkbox"/>				\$0.00	
TOTAL FEES ENCLOSED =				\$970.00	
				Amount to be: refunded	\$
				charged	\$


☒ A check in the amount of **\$970.00** to cover the above fees is enclosed.

☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **06-1050** A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

TSAO, Y. Rocky Fish & Richardson P.C. 225 Franklin Street Boston, Massachusetts 02110-2804 United States of America	 SIGNATURE Y. Rocky TSAO NAME 34,053 REGISTRATION NUMBER 23 March 2000 DATE
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : William Harold Jay

Art Unit : Unknown

Serial No. :

Examiner : Unknown

Filed : March 23, 2000

Title : ION EXCHANGE

BOX PCT

Assistant Commissioner for Patents

Washington, D.C. 20231

Int'l Patent Application: PCT/AU98/00811

Int'l Filing Date: 25 September 1998

PRELIMINARY AMENDMENT

Prior to examination, please amend the application as follows:

In the Claims:

In claim 3, line 1, delete "either" and "or claim 2".

In claim 4, line 1, replace "any one of claims 1 to 3" with -claim 1--.

In claim 5, line 1, replace "any one of claims 1 to 4 with -claim 1--.

Add the following new claims:

--7. An ion exchange material according to claim 2 wherein the ion exchange medium is in the form of a bead, resin, fibre, foam, liquid or other convenient form.

CERTIFICATE OF MAILING BY EXPRESS MAIL

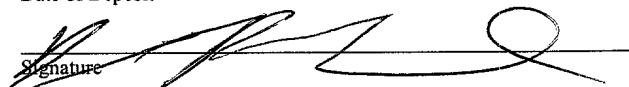
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I hereby certify under 37 CFR §1.10 that this correspondence is being deposited with the United States Postal Service as Express Mail Post Office to Addressee with sufficient postage on the date indicated below and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

March 23, 2000

Date of Deposit

Signature



Jonathan R. Howard

Typed or Printed Name of Person Signing Certificate

8. An ion exchange material according to claim 2 wherein the ion exchange medium is in liquid form and is imbibed into a solid sorbent for embedding into the superabsorbent polyurethane foam.

9. An ion exchange material according to claim 3 wherein the ion exchange medium is in liquid form and is imbibed into a solid sorbent for embedding into the superabsorbent polyurethane foam.

10. An ion exchange material according to claim 2 wherein the ion exchange medium is in the form of an emulsion or suspension for imbibing into the superabsorbent polyurethane.

11. An ion exchange material according to claim 3 wherein the ion exchange medium is in the form of an emulsion or suspension for imbibing into the superabsorbent polyurethane.

12. An ion exchange material according to claim 4 wherein the ion exchange medium is in the form of an emulsion or suspension for imbibing into the superabsorbent polyurethane.--

REMARKS

Applicants have amended the dependency of the claims to preclude a rejection under 35 U.S.C. § 112, fifth paragraph, which provides in part that "[a] multiple dependent claim shall not serve as a basis for any other multiple dependent claim." No new matter has been added by the above amendments.

Applicant : William Harold Jay
Serial No. :
Filed : March 23, 2000
Page : 3

Attorney's Docket No.: 11750-002001

Applicant submits that all of the claims are now in condition for examination, which action is requested. Please apply any other charges or credits to Deposit Account No. 06-1050.

Respectfully submitted,

Date: 3-23-00

Y. Rocky Tsao
Y. Rocky Tsao
Reg. No. 34,053

Fish & Richardson P.C.
225 Franklin Street
Boston, MA 02110-2804
Telephone: (617) 542-5070
Facsimile: (617) 542-8906

20041626.doc

Applicant or Patentee: William Harold Jay
Serial or Patent No.: 09/509,301
Filed or Issued: March 23, 2000
For: ION EXCHANGE

Attorney's 11750/
Docket No.: 002001

VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY STATUS
(37 CFR 1.9(f) and 1.27(c)) - SMALL BUSINESS CONCERN

I hereby declare that I am

- ☐ the owner of the small business concern identified below:
☒ an official of the small business concern empowered to act on behalf of the concern identified below:

NAME OF CONCERN Holbray Pty Ltd
ADDRESS OF CONCERN 566 David Street, Albury NSW 2640

I hereby declare that the above identified small business concern qualifies as a small business concern as defined in 13 CFR 121.3-18, and reproduced in 37 CFR 1.9(d), for purposes of paying reduced fees under section 41(a) and (b) of Title 35, United States Code, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby declare that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the invention, entitled
ION EXCHANGE by inventor(s)

described in William Harold Jay

- ☒ International patent application No PCT/AU98/00811 filed 25 September 1998
☐ the specification filed herewith
☒ application serial no. 09/509,301; filed March 23, 2000
☐ patent no. , issued

If the rights held by the above identified small business concern are not exclusive, each individual, concern or organization having rights to the invention is listed below* and no rights to the invention are held by any person, other than the inventor, who could not qualify as a small business concern under 37 CFR 1.9(d) or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e). *NOTE: Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities. (37 CFR 1.27)

NAME
ADDRESS
☐ INDIVIDUAL ☐ SMALL BUSINESS CONCERN ☐ NONPROFIT ORGANIZATION

NAME
ADDRESS
☐ INDIVIDUAL ☐ SMALL BUSINESS CONCERN ☐ NONPROFIT ORGANIZATION

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING ROBERT SAMUEL ALLEN
TITLE OF PERSON OTHER THAN OWNER SOLE DIRECTOR/SECRETARY
ADDRESS OF PERSON SIGNING 566 DAVID STREET
SIGNATURE [Signature] DATE 26/4/2000

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ION EXCHANGE

The present invention relates to ion exchange, in particular to ion exchange materials embedded in a polyurethane matrix. The present invention also relates to a process for the recovery of metal cations and anions from solutions and slurries.

Ion exchange resins are generally manufactured in bead or particulate form from polymers such as polystyrene-divinyl benzene, acrylic, or phenol-formaldehyde condensates has been proposed that ion exchange fibres can be produced from either polyacrylonitrile onto which active ligands can be attached, or polypropylene fibres on to which polystyrene-divinyl benzene can be grafted. Polyurethane foams have been proposed in PCT/AU93/00312 and PCT/AU94/00793 which are incorporated herein in their totality by reference.

Ligands can be attached to the surface of the particular ion exchange resins or fibres by conducting one or more suitable chemical reactions.

Commercially manufactured resins have several disadvantages, including small particle size to provide a large surface-to-volume ratio, often lower selectivity for one metal ion species over other metal ion species prevalent in leach liquors and pK_a values which prevent the resin loading anions at pH values above about 10. Additional ligand capacity is provided by making the resin beads macroporous. This may be achieved by incorporating one or more porogens into the resin system during the polymerisation step. Such macroporosity, can lead to increased shattering of the beads in industrial processes.

The bulk density of the beads are not readily modified. Thus, the ion exchange beads being offered for application in for example, the gold industry have a tendency to float on the surface of the pulp during the cyanidation step. It is reported that this has led to loss of gold due to pilferage of the loaded beads.

In an effort to overcome this disadvantage, U.S. Patent 4,284,511 which is incorporated here

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by reference, describes the addition of magnetic material, particularly finely divided particles of a non-corrosive, iron-chrome alloy to raise the bulk density of the polymer. This addition is proposed to be used with activated carbon, and polyurethane and similar materials when used in ion exchange columns, and in particular, in fluidised bed towers to enable higher fluid
5 flow rates to be achieved.

Other disadvantages of currently available ion exchange resins for metal ion recovery include:

- (a) purchase cost is high,
10
- (b) the present need for fine sized beads (in order to achieve a significant concentration of ligands) renders it difficult to recover them from pulps by screening,
- (c) stripping kinetics are slower and a more complex stripping regime is often required to
15 effectively recover the metal ion for electrowinning.

We have now found that by embedding an ion exchange material in a superabsorbent polyurethane foam we are able to achieve superior ion exchange performance. The present invention accordingly provides an ion exchange material comprising a superabsorbent
20 polyurethane foam having an ion exchange medium contained therein.

The present invention also provides a process for the extraction of metal anions and cations from solutions and/or slurries including the steps of:

- 25 (a) contacting a metal ion-containing solution with an ion exchange material comprising a superabsorbent polyurethane foam having an ion exchange medium contained therein;
- (b) separating the ion exchange material from the solution and/or slurry; and
- 30 (c) recovering the sorbed metal ions from the ion exchange medium.

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These superabsorbent, hydrophilic polyurethane polymers are chemical entities which are well known to those skilled in the art. Methods for the preparation or application of these polymers are typically described in U.S. Patent Numbers

3,793,241; 3,854,535; 3,861,993; 3,890,254; 3,900,030; 3,903,232; 3,904,557; 4,110,508;
5 4,127,516; 4,137,200; 4,158,087; 4,160,076; 4,181,770; 4,266,043; 4,292,412; 4,314,034;
4,365,025; 4,337,645; 4,384,050; 4,384,051; 4,717,738; 4,725,628; 4,731,391; 4,740,528;
4,789,720; 4,798,876; 4,828,542; 5,065,752; 5,296,518; 5,591,779 and 5,624,971, which are incorporated herein by reference.

- 10 The procedure for the manufacture of the prepolymers described in the above patents is either given within the description, or can be produced according to typical procedures as described in various publications relating to polyurethane chemistry, or as disclosed in U.S. Patent Nos. 2,726,219; 2,948,691; 2,993,013; 3,805,532 and 4,137,200.
- 15 In U.S. Patent 4,725,629 a superabsorbent polyurethane foam based upon an interconnecting polymer network of a crosslinked polyurethane and a cross-linked addition polymer containing a plurality of chain segments made up of functional groups containing repeating units which may be the same or different. These superabsorbent polymers are recommended for the manufacture of absorbent articles, especially disposable absorbent articles, such as
- 20 nappies, sanitary napkins, bedpads, incontinent pads, and the like.

Superabsorbent polyurethane foams preferably derived from an isocyanate-terminated poly(oxyalkylene) polyol having an isocyanate functionality greater than two and containing an addition polymer such as acrylamides, acrylate and methacrylate salts, etc. are disclosed

25 in U.S. Patent 4,731,391

British Patent 1,209,058 discloses a hydrophilic polyurethane foam in which a polyether polyol containing a block of ethylene oxide capped with propylene oxide to obtain hydrolytic stability is reacted with a polyisocyanate. Only small quantities of water are used. The foams

30 produced by this method have very poor water absorbing properties.

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A superabsorbent polyurethane foam into which microcapsules of active ingredients are formed is described in U.S. Patent 4,828,542. The hydrophilic polyurethane prepolymer is foamed by mixing with water in the range of at least approximately 0.2/1 or greater and
5 preferably 1/1 or greater.

U.S. Patent 5,065,752 describes a superabsorbent, hydrophilic foam composition for wound dressings. The polyurethane foam is produced by the in-situ reaction product of an isocyanate-capped polyether prepolymer, a polymeric hydrophilic agent capable of absorbing water (such
10 as starch grafted copolymers of acrylate salts, or acrylamide salts), an adjuvant comprising a water-soluble alcohol, a wetting agent, and water.

U.S. Patent 5,591,779 discloses a process for preparing a superabsorbent polyurethane foam by reacting a suitable polyurethane prepolymer with water in the presence of a superabsorbent
15 polymer. The polyurethane prepolymer contains an oxyethylene content of at least 50% by weight. The amount of water required being 15 to 500 parts by weight of the weight of the prepolymer. At the start of the reaction, the temperature of the water being 10°C to 50°C higher than the temperature of the prepolymer.

20 The ion exchange medium may be any convenient ion exchange medium suitable for sorbing the desired metal ions from the solution and/or slurry. The ion exchange medium may be in the form of a bead, resin, fibre, foam, liquid or other convenient form.

Ion exchange mechanisms generally involve the exchange of ions in solution with the counter
25 ions associated with the ligands present in the extractant. The extractant may be either an insoluble solid inorganic or organic material, or a water-insoluble organic molecule. Thus, the desired extractant therefore contains anionic, cationic, or chelating ligands capable of recovering the desired metal ion from either solutions or from slurries.

30 Normally a metal ion exists in an aqueous solution as a hydrated ion with little or no tendency

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to transfer to an organic phase. To enable an ion to transfer into an organic phase it is generally required that its charge must be neutralised and some, or all of its water of hydration has to be replaced by some other molecule or ion. For example, as reported by Irving and Damodaran the aurocyanide anion is generally weakly hydrated compared to other cyano-metallic complexes. Thus, its affinity for organic matrices relative to other more strongly hydrated anions, will be greater. A study on ionic mobilities in the Nernst layer has shown that the aurocyanide complex is significantly smaller and less hydrated than other cyano complexes. Examination of the hydration and ion pairing of the $\text{Au}(\text{CN})_2^-$ complex in aqueous solution does however require further investigation. Therefore, for a metal ion to be removed from the aqueous phase, these conditions can be met by:

- (a) complexing the ion with an ion of opposite charge to form a neutral species, which at the same time replaces some or all of the water of hydration around the metal ion,
 - (b) by formation of ion-association complexes which also provide for the formation of a neutral species with the extractant,
 - (c) by replacing the water of hydration with molecules of the extractant.
- An ion exchange medium, thus, may be a polymeric material in particulate, bead, fibre or foam form which carries a fixed positive or a fixed negative electrical charge. This electrical charge is balanced by ions of opposite sign, called counter ions. In solution, these counter ions are free to move within the resin matrix and therefore can be replaced, or exchanged, by other ions of the same sign. Thus systems employing chelating and acidic extractants are cation-exchange reactions, and those employing anion exchange systems are anion-exchange reactions.

Extractants containing C-O bonds are electron donating compounds, but alcohols being amphoteric, exhibit both donor and acceptor properties and resemble water in many ways. Thus, the formulation of superabsorbent polymers based upon poly(oxyethylene) glycol, and

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if required sulphonic groups in the polymer structure, will enhance metal ion transport. Alcohols such as pentanol, n-hexanol, 2-ethylhexanol, isodecanol, dodecanol, tridecanol, hexadecanol, octadecanol; phenols such as heptylphenol, octylphenol, nonylphenol and dodecylphenol may be included into these superhydrophilic foams to improve solvation and also metal ion transport. The need for hydrophilicity in the polymer to enhance the metal ion loading is demonstrated by Chiariza, R., et al., Diphonix® resin: A review of its properties and applications, Sep. Sci. and Technol - (1997), 32 (1-4), 1-35.

10 The preferred aromatic isocyanates are 2,4- and 2,6- toluene diisocyanates and methylene-bridged polyphenyl polyisocyanate mixtures which have a functionality of from about two to about four. These latter isocyanate compounds are generally produced by the phosgenation of corresponding methylene-bridged polyphenyl amines, which are conventionally produced by the reaction of formaldehyde and primary aromatic amines, such as aniline, in the presence
15 of hydrochloric acid and/or other acidic catalysts. Known processes for preparing polyamines and corresponding methylene-bridged polyphenyl polyisocyanates therefrom are described for example in U.S. Patent Nos. 2,683,730, 2,950,263, 3,012,008, 3,344,162 and 3,362,979.

Most preferred methylene-bridged polyphenyl polyisocyanate mixtures used herein contain
20 about 20 to about 100 weight percent methylene diisocyanate isomers, with the remainder being polymethylene polyphenyl isocyanates having higher functionalities and higher molecular weights. Typical of these are polyphenyl polyisocyanate mixtures containing about 20 to 100 weight percent methylene diphenyldiisocyanate isomers, of which 20 to about 95 weight percent thereof is the 4,4' -isomer with the remainder being polymethylene polyphenyl
25 polyisocyanates of higher weight and functionality of from about 2.1 about 3.5. These isocyanate mixtures can be prepared by the process described in U.S. Patent 3,332,979.

A commercially available MDI compound with especially desirable properties is Isonate 143L which is produced by reacting MDI to form the carbodiimide and this material in turn then
30 reacts to form a tri-functional cycloadduct. The mixture of MDI, the carbodiimide and the

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cycloadduct are in equilibrium. The mixture contains a major amount of pure diphenylmethane diisocyanate and minor amounts of carbodiimides and trifunctional cycloadducts of diphenylmethane diisocyanate. As described, the term derivatives of diphenylmethane diisocyanate means products that have been made from MDI as a starting material. It includes adducts dimers, and trimers.

Other compounds which are useful are the isocyanate equivalents which produce the urethane linkages such as the nitrile carbonate, including the adiponitrile carbonate.

10 Also, both ethers and ketones allow a high degree of metal hydration in the solvent phase. For example, in the extraction of ferric chloride into ether, five molecules of water are associated with the extracted metal complex in the solvent phase and solvation numbers as high as 12 have been reported. Thus, superhydrophilicity enables these water molecules to be rapidly transported through the polymer to the reactive sites.

15

The preferred components include a diol having greater than about 80% by weight of poly(oxyethylene) groups (such as PEG 1000) to provide the water-absorbing property, trimethylolpropane as the crosslinking agent, suspending or thickening agents and the isocyanate used to cap or terminate the polyol is as described above.

20

The poly(oxyethylene) polyol may have a molecular weight of about 200 to about 20,000 and preferably between about 600 to about 6,000 and most preferably about 1000 to about 1400, with a hydroxyl functionality of about 2 or greater, but preferably from about 2 to 6 and most preferably, 2.

25

The chain extenders which may be added to provide crosslinking strength to the foam are relatively short, low molecular weight monomeric polyols having three or four hydroxyl equivalents per mole. Such materials include glycerol, trimethylolpropane, trimethylolethane, triethanolamine, pentaerithritol, or mixtures thereof.

30

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Suspending or thickening agents include acrylic acid-based polymers such as Carbopol 934 and Carbopol 940. A neutralising agent such as sodium or ammonium hydroxide can be added.

- 5 The capping or termination reaction between the isocyanate and the polyol may be carried out in an inert moisture-free atmosphere such as under a nitrogen blanket, at atmospheric pressure at a temperature in the range of about 0°C to about 120°C for a period of time of up to about 24 hours depending upon the temperature and the degree of agitation and cooling or heating applied to the reactor.

10

Superabsorbent microcellular resins and foams differ from the above polyurethane foams in that they are normally produced by the reaction of a suitably formulated isocyanate terminated polymer with a very significant excess of water. The polyol portion of the polymer is generally based upon poly(oxyethylene) glycol, and the isocyanate component is generally

- 15 TDI, MDI or MDI -based isocyanate or mixtures of both isocyanates.

Another very desirable property of the instant foams is the elimination of silicone surfactants from the formulation. It has been observed that these nonionic silicone-based raw materials are specifically formulated so that they migrate to the surface of the rising foam to control the
20 surface tension, promote nucleation and stabilise the rising foam by reducing stress concentrating in thinning cell-walls and counteract any defoaming effects caused by the presence of added, or generated/solid matter. Thus, these polymers remain at the surface of the cured polyurethane foam and interfere with subsequent interpenetration of a second polymer or surface reactions conducted on the polyurethane foam cell walls.

25

The use of water soluble or water dispersable- surface active agents in urethane-urea foams is taught in U.S. Patent Nos. 3,890,254 and 4,160,076 to be critical to the attainment of many useful properties. Whereas, in U.S. Patent No. 5,296,518 it was recognised that the choice of certain isocyanate-capped high molecular weight molecules can be used in place of
30 these surfactants. Being water soluble, and not taking part in the chemical reaction, they can

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be leached out of the foam. Thus, the presence of these surface active agents does not interfere with subsequent surface reaction such as interpenetration of a second polymer system.

- 5 The level of surfactant may be varied from 0% to about 5% based upon the total water content of the formulation. If low levels of surfactant are used higher density foams will generally result. Such polymers will have advantage in applications in which the final product is required to offer improved abrasion resistance. In the present invention the Pluronic series of surfactants manufactured by BASF are preferred, with Pluronic L62 being particularly preferred in this
10 aspect.

Thermal reticulation whereby the windows or membranes are removed from individual cells or bubbles which make up the foam structure. Reticulation results in a foam preferably having at least 95% of open cells and most preferably 99% open cells. Thermal reticulation
15 of polyurethane foam is a known procedure to those skilled in the art and as disclosed for example is U.S. Patent Nos. 3,171,820 and 3,875,025 and 3,175,030. Reticulation is achieved by providing a combustible mixture of an oxidiser material and an oxidisable material within the cells of the foam and then igniting the combustible mixture whereupon the cell windows or membranes are destroyed. It is also possible to swell the polyurethane foams
20 in an organic solvent to increase the cell size.

Thus, as disclosed in U.S. Patent 4,985,467, the skeletal structure is completely open, and with such a structure, it will more rapidly absorb large amounts of liquid than an a non-reticulated cellular foam.

25

Poly(ethylene oxide) derivatives are good solvents for metal ions because of the Lewis-base nature of the lone pairs on the oxygen atom. Macrocycles based on the ethylene oxide unit, the crown ethers, are amongst the strongest known complexing agents for cations. The reason for this is twofold, namely, the rings formed by ethylene oxide units tend to place oxygen
30 atoms in favourable positions for the formation of coordination bonds with metal cations; and

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secondly, the excellent solvating properties of poly(ethylene oxide) .

To produce the desired superabsorbent ion exchange resins, several different methods may be adopted. In one preferred method, commercially produced solid ion exchange polymers
5 may either be comminuted to reduce their particle size, or they may be used directly in the resin forming step, details of which appear below.

Alternatively, an another preferred method, organic liquid ion exchange materials may be imbibed into a solid sorbent in a suitable form such as particulates, sheets, fibres, foams.
10 Such solid sorbents include styrene-divinyl benzene, acrylic, phenolformaldehyde, polyvinyl chloride, carbon, zeolites, vermiculite, etc and then incorporated into the superabsorbent resin.

Whilst the extractants may be imbibed into pulverised materials, it is also acceptable that highly
15 porous materials, such as activated carbon, granules be used. The extractant can be imbibed into these materials, preferably under reduced pressure to remove entrapped air form within the porous material. A dilute coating of the prepolymer, such as is described in Example 7, may then be applied to the outer surface of the beads.

20 A further method is to melt a suitable wax such as petroleum wax, beeswax, a mixture of waxes etc., in hot water containing a suitable surfactant such as Pluronic L62 manufactured by BASF and add the liquid ion exchange or extractant mixture whilst stirring to form an emulsion. Continue stirring during cooling to room temperature to from an aqueous emulsion dispersion of the organic mixture in water. This aqueous emulsion is then used as part of the
25 aqueous phase for production of the superhydrophilic polymer.

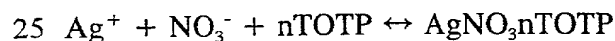
TBP addition to an uncharacterised polyurethane foam for the recovery and separation of nickel and palladium is described by Braun and Farag, Talanta (1972), 19,828-830. This foam would not have provided sufficient hydrophilicity as enunciated in the present
30 disclosure.

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A number of phosphates, including di(2-ethylhexyl) phosphate, and particularly tri-n-butyl phosphate (TBP) have been extensively employed in solvent extraction systems for metal ions. TBP has been included in a number of patents relating to gold recovery from chloride and cyanide solutions. It is used in industrial process to remove arsenic from copper solutions. It is proposed as a suitable extractant for zinc from acid solution.

As a general rule, the extractive power of phosphorous containing extractants increases with an increase in the number of carbon-phosphorous bonds over the series, phosphate-phosphonate-phosphine oxide. The solubility of neutral organophosphorus compounds in water decreases in the order phosphine oxides > phosphinates > phosphonates > phosphates. This is as a result of the increasingly polar nature of the phosphoryl group. It should be noted that in acid solutions these extractants have low solubility, but as the pH increases, so solubility increases. It is known that the phosphoryl oxygen forms hydrogen bonds with water, and the bond energy is approximately 5kcal/mole. The more basic oxygen in a phosphonate gives a hydrogen bond energy of about 7-8 kcal/mole.

Dialkyl phosphorodithioic acids, phosphonates, dialkylthiophosphate, sulphur-containing methyl phosphonates and ketophosphonates and the trialkyl thiophosphates have been shown to be highly selective for gold, silver and mercury. Triiso-octyl thiophosphate and tri-n-butyl thiophosphate are similar to their trialkyl phosphate counterparts except that the P=O has been replaced by a P=S group. The semipolar sulphur atom is the sole structural difference between the two types. Handley and Dean proposed that the trialkyl thiophosphates probably act by solvating an electrically neutral ion association complex.



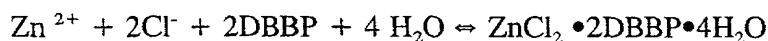
The ion association bonding occurs through the P=S group. The semipolar sulphur atom has very little electron donating ability, and will bond only to ions of high field strength. Silver and mercury fit this criteria and also are amongst those metals which prefer sulphur-containing ligands. These extractants have been shown to reduce Au (III) to Au°.

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Extraction of cadmium, zinc, and mercury have been demonstrated to be possible with thiophosphorus compounds containing a P-SH group. The affinity of these metals for sulphur increases in the order zinc < cadmium < mercury. The extractants studied included di-n-butyl thiophosphite (DBTP) and the di-n-butyl ester of 2-hydroxypropan-2-thiophosphonic acid (DBPrPS). It has been reported that mercury and gold (III) chloride are extracted from hydrochloric acid solutions with triisobutylphosphine sulphide (Cyanex 471X). This extractant is particularly selective for silver and for the separation of palladium and platinum.

In extraction of metal ions from acidic media generally two molecules of TBP are involved in the extracted species. Furthermore, as the acid concentration increases so extraction of metal increases until a maximum is reached above which extraction decreases.

In a similar manner, dibutyl butyl phosphonate (DBBP) has been employed for the extraction of gold, and PGM's, and for zinc. DBBP has a high selectivity and loading capacity for zinc in chloride solutions resulting from ferric chloride leaching of a complex sulphide ore. Extraction was found to be independent of pH. He reported that two moles of DBBP react with one mole of zinc. As a solvating extractant, extraction occurs as the extractant molecules replace water molecules in the primary hydration sheath of the extracted species. From the determination of free activities of water and free chloride ions it was shown that four water molecules and two chloride ions are involved for each extracted zinc species. The extraction reaction may be written as follows:



DBBP may form dimers at concentrations higher than $3.7 \times 10^{-1} \text{ mol/dm}^3$ and thus at lower concentrations the plot of Log [DBBP] versus Log E a straight line with a slope of two is obtained. At concentrations higher than $3.7 \times 10^{-1} \text{ mol/dm}^3$ the slope is greater than two possibly because the extraction equilibrium changes in favour of extraction when DBBP dimers form. DBBP may form dimers at higher free DBBP concentrations in a manner similar to that reported by Burger for tributyl phosphate.

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Industrial applications of ion exchange resins are many, particularly in the treatment of boiler feedwater. U.S. Patent 4,069,119 which is incorporated here by reference, describes the application of ion exchange resins to recover copper from dilute solutions emanating from vat
5 leaching of copper ores. This patent describes the beneficial effect of recovery from solutions containing significant levels of dissolved silica. This patent describes ion exchange resins in bead form, including polyurethane foams and porous beads impregnated with conventional organic solvent extraction agents to produce materials which may be employed as ion exchange beads in this application.

10

Other methods for the preparation or application of these polymers are typically describes in US Patent Numbers 3,793,241; 3,845,535; 3,861,993; 3,890,254; 3,900,030; 3,903,232; 3,904,557; 4,110,508; 4,127,516; 4,137,200; 4,158,087; 4,160,076; 4,181,770; 4,226,043; 4,292,412; 4,314,034; 4,365,025; 4,337,645; 4,384,050; 4,384,051; 4,717,738; 4,725,628;
15 4,731,391; 4,740,528; 4,789,720; 4,798,876; 4,828,542; 5,065,752; 5,296,518; 5,591,779 and 5,624,971, incorporated herein by reference.

The procedure for the manufacture of the prepolymers described in the above patents is either given within the description, or can be produced according to typical procedures as described
20 in various publications relating to polyurethane chemistry, or as disclosed in US Patent Nos. 2,726,219; 2,948,691; 2,993,013; 3,805,532 and 4,137,200.

Advantageously the ability to incorporate large volumes of water into the formulation provides an opportunity to incorporate water-based polymer emulsions directly into the polymer. This
25 cannot generally be achieved by the application of conventional polyurethane foams. Water-based polymers eliminate the requirement for solvents in the polymer preparation and therefore eliminate the need to remove and capture environmentally undesirable solvents. Typically, such emulsions may be water-based emulsion resulting from the reaction of vinylidene diphosphonic acid with polyvinylpyridine. Such a product, when incorporated into the superhydrophilic
30 polyurethane foam, any offer exceptional selectivity for FE(III) in the presence of Cu(II) in acid solutions commonly encountered in copper electrowinning tankhouse bleed streams.

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The present invention will now be further described by the following non-limiting examples.

EXAMPLES

5

EXAMPLE 1.

A hydrophilic prepolymer "Prepolymer" was prepared by reacting together a 1000 MW poly(oxyethylene) glycol with toluene diisocyanate to produce an isocyanate-terminated prepolymer and then adjusted by the addition of MDI to produce a finished product with a free

10 NCO content of 9.5%.

PEG1000	100 pbw
TDI	44 pbw
MDI	to provide a Free NCO content of 9.5%

15

Into a suitable mixing container were added:

	Separan Solution (1 % in water)	25g
	Water	75g
20	Pluronic L62	1.0g
	Vitrocele V912 (ion exchange beads)	20g
	Ferrosilicon powder	20g
	Dyestuff	1 drop

25 The ingredients were thoroughly mixed together and then poured into a second container containing 50 grams of the following mixture:

Prepolymer	10g
Isonate 143L	1.5g

30

The mixture was allowed to rise to form a foam. Pieces were then cut from this foam for metal

- 15 -

ion loading. Alternatively, the mixture was allowed to react and cure between two sheets of waxed paper and constrained in such a manner that a sheet of about 5 mm in thickness was obtained. This sheet was cut to size.

- 5 The polymer produced was used to remove gold cyanide and copper apinade from aqueous solutions and slurries.

EXAMPLE 2

In the examples in which a liquid organic extract was used, the following procedure was
10 adopted:

XAD-16 (Manufactured by Rohm and Haas) milled	10g
LIX 841 (Manufactured by Henkel Corporation)	10g
Polyethylene glycol 1000	2g

15

The solid resin and the organic extractant were combined together and heated to about 35°C with constant stirring. Once the extractant was fully imbibed into the resin, the PEG1000 was added and stirring continued. A dry powder was obtained.

- 20 This powder was then mixed with the following:

Powder	15g
Ferrochrome	10g
Water	20g
1 % Separan Solution	5g
25 Pluronic L62	0.75g

To this mixture was added:

Prepolymer	20g
Isonate 143L	5g

30

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The mixture was allowed to rise to form a foam. Pieces were then cut from this foam for metal ion loading. Alternatively, the mixture was allowed to react and cure between two sheets of waxed paper and constrained in such a manner that a sheet of about 5 mm in thickness was obtained. This sheet was cut to size.

5

The polymer produced was used to remove copper ions from aqueous solutions.

EXAMPLE 3

Into a suitable mixing container was added:

10	Separan solution (1% in water)	6g
	Water	60g
	Pluronic L62	0.75g
	Ion exchange beads with guanidine functionality	20g
	Liquid guanidine-based extractant	5g
15	Pentanol	5g
	PEG1000	5g
	Ferrosilicon powder	5g
	Dyestuff	1 drop

20 The ingredients were thoroughly mixed together and then poured into a second container containing 40 grams of the following mixture:

Prepolymer	180g
Isonate 143L	30g

25

EXAMPLE 4

0.1 g of each of the ion exchange polymers described in Examples 1 and 3, Vitrocele V912 and guanidine resin (based upon its dry weight) was contacted with 500 mls of a solution containing 5 ppm gold (as gold cyanide) + 200 ppm of CN^- (as sodium cyanide), the pH being adjusted to 10.6. At the specified time intervals, samples of the aqueous solution were withdrawn and analysed by AAS technique. The results obtained are given in Figure 1.

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EXAMPLE 5

The experiments conducted in Example 4 were repeated but in this case, the gold cyanide was replaced with 5 ppm of copper as copper cyanide. The results obtained are give in Figure 2.

5 EXAMPLE 6

A polymer was prepared by:

Styrene-divinyl benzene resin (XAD-7 milled)	10g
LIX 84I	10g

- 10 The solid resin and the organic extractant were combined together and heated to about 35°C with constant stirring. Once the extractant was fully imbibed into the resin, a dry powder was obtained.

This powder was then mixed with the following:

15	Powder	20g
	Water	30g
	Pluronic L62	0.75g

To this mixture was added:

20	Prepolymer	20g
----	------------	-----

The mixture was allowed to rise and cure.

EXAMPLE 7

- 25 A reticulated polyurethane foam was imbibed with 25% of LIX 84I and then dipped in a mixture of Prepolymer:water of 1:5, drained and allowed to cure.

EXAMPLE 8

- 30 The LIX 84I superhydrophilic foams prepared as described in Examples 2, 6 and 7 were compared with equivalent weights of commercially available copper-selective ion exchange resins as follows:

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A feed solution containing 77 ppm copper, 570 ppm iron (as Fe (III)) at pH 2 was contacted with each of the polymers, the experiments being conducted at room temperature.

After 20 hours the loadings of copper obtained were:

	Cu	Fe
5		
Amberlite IR-120 (sulphonic acid functionality)	4mg/g	95mg/g
Amberlite IMAC HP 333 (carboxylic acid funct.)	0mg/g	65mg/g
Amberlite IRC-718 (iminodiacetic acid funct.)	11mg/g	75mg/g
Example 2	11mg/g	20mg/g
10 Example 6	23mg/g	25mg/g
Example 7	8mg/g	0mg/g

The results given in Examples 1, 3, 4 and 8 indicate that on a ligand functional basis, the superhydrophilic foams show faster loading kinetics and improved loading when compared with the unmodified and commercially available ion exchange resins.

The results given in Examples 2, 6, 7 and 8 clearly show that the amidoxime-based (LIX 84I) superhydrophilic polymers showed significantly better loading of copper and exceptional rejection of iron. The carboxylic acid resin initially loaded copper, but this was rapidly replaced by iron. The sulphonic acid loaded iron in preference to copper.

CLAIMS

1. An ion exchange material comprising a superabsorbent polyurethane foam having an ion exchange medium contained therein.

5

2. An ion exchange material according to claim 1 wherein the ion exchange medium is selected for sorbing desired metal ions from a solution and/or slurry.

3. An ion exchange material according to either claim 1 or claim 2 wherein the ion
10 exchange medium is in the form of a bead, resin, fibre, foam, liquid or other convenient form.

4. An ion exchange material according to any one of claims 1 to 3 wherein the ion
15 exchange medium is in liquid form and is imbibed into a solid sorbent for embedding into the superabsorbent polyurethane foam.

5. An ion exchange material according to any one of claims 1 to 4 wherein the ion
exchange medium is in the form of an emulsion or suspension for imbibing into the
superabsorbent polyurethane.

20

6. A process for the extraction of metal anions and cations from solutions and/or slurries including the steps of:

(a) contacting a metal ion-containing solution with an ion exchange material comprising a
25 superabsorbent polyurethane foam having an ion exchange medium contained therein;

(b) separating the ion exchange material from the solution and/or slurry; and

(c) recovering the sorbed metal ions from the ion exchange medium.

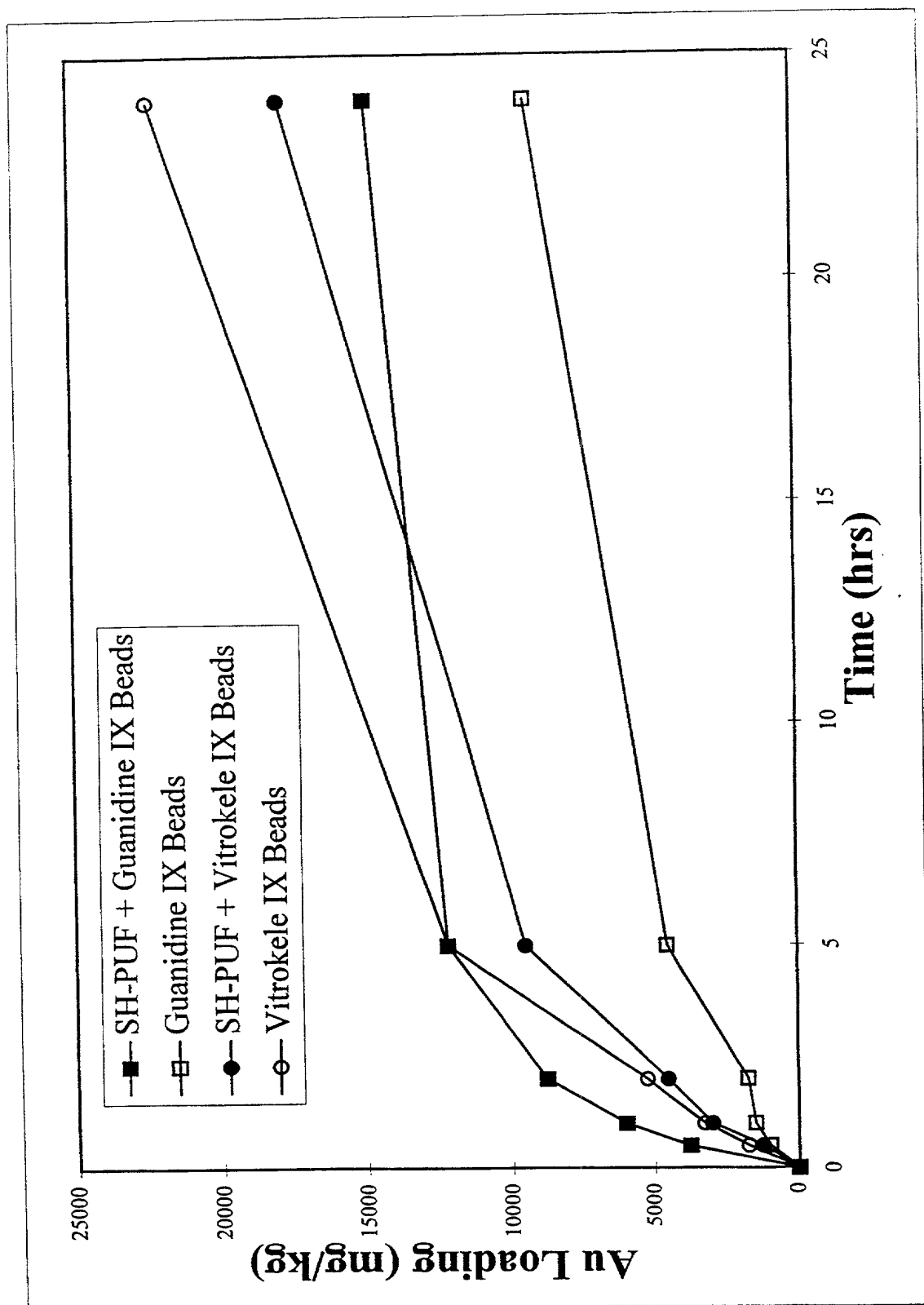


FIGURE 1

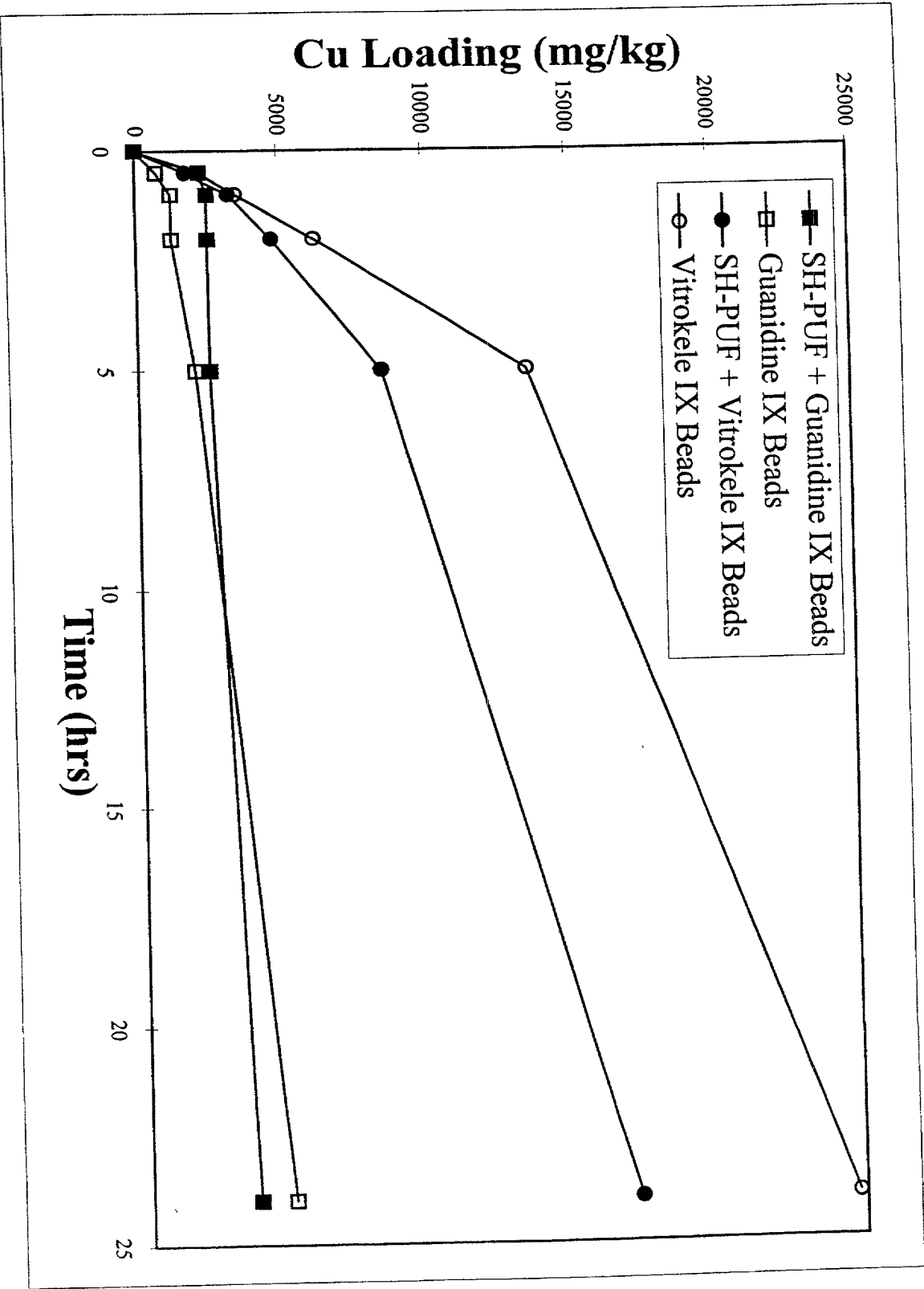


FIGURE 2

FIG. 2 is a line graph showing the Cu loading capacity of three different bead types over time. The y-axis represents Cu loading in mg/kg, ranging from 0 to 25,000. The x-axis represents time in hours, ranging from 0 to 25. The legend indicates three bead types: SH-PUF + Guanidine IX Beads (filled squares), Guanidine IX Beads (open squares), and SH-PUF + Vitrokele IX Beads (filled circles). The graph shows that SH-PUF + Guanidine IX Beads have the highest loading capacity, reaching approximately 22,000 mg/kg at 24 hours. Guanidine IX Beads reach approximately 6,000 mg/kg at 24 hours. SH-PUF + Vitrokele IX Beads reach approximately 18,000 mg/kg at 24 hours.

09/509 301

COMBINED DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled ION EXCHANGE

the specification of which

☐ is attached hereto.

☒ was filed on 3/23/00 as Application Serial No. 09/509,301.

☒ was described and claimed in PCT International Application No. PCT/AU98/00811

filed on 25 Sept. and as amended under PCT Article 19 on 1998.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose all information I know to be material to patentability in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

COUNTRY	APPLICATION NO.	FILING DATE	PRIORITY CLAIMED
Australia	P09462	25 September 1997	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
PCT	PCT/AU98/00811	25 September 1998	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
			<input type="checkbox"/> Yes <input type="checkbox"/> No
			<input type="checkbox"/> Yes <input type="checkbox"/> No
			<input type="checkbox"/> Yes <input type="checkbox"/> No

20 I hereby appoint the following attorneys and/or agents to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith: John F. Hayden, Reg. No. 37,640; John C. Phillips, Reg. No. 35,322; Linda Liu Kordziel, Reg. No. 39,732; Eldora L. Ellison, Reg. No. 39,967; Carl B. Wischhusen, Reg. No. P-43-279; William E. Booth, Reg. No. 28,933; Ruffin B. Cordell, Reg. No. 33,487; David L. Feigenbaum, Reg. No. 30,378; John W. Freeman, Reg. No. 29,066; Timothy A. French, Reg. No. 30,175; Alan H. Gordon, Reg. No. 26,168; John F. Land, Reg. No. 29,554; G. Roger Lee, Reg. No. 28,963; Ralph A. Mittelberger, Reg. No. 33,195; John B. Pegram, Reg. No. 25,198; Rene D. Tegtmeyer, Reg. No. 33,567; Hans R. Troesch, Reg. No. 36,950; Dorothy P. Whelan, Reg. No. 33,814; Charles C. Winchester, Reg. No. 21,040; Thomas G. Woolston, Reg. No. 40,235.

Address all telephone calls to John F. Hayden at telephone number 202/783-5070.

Address all correspondence to John F. Hayden, Fish & Richardson P.C., 601 13th Street, N.W., Washington, D.C. 20005.

COMBINED DECLARATION AND POWER OF ATTORNEY CONTINUED

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patents issued thereon.

Full Name of Inventor William, Harold Jay
Inventor's Signature [Signature] Date 28/4/2000
Residence 64 Turana Street, Doncaster, VIC 3108
Citizenship Australian
Post Office Address as above

Full Name of Inventor _____
Inventor's Signature _____ Date _____
Residence _____
Citizenship _____
Post Office Address _____

Full Name of Inventor _____
Inventor's Signature _____ Date _____
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